EP 1 323 685 A2

Publishing Date: July 2, 2003
Application Date December 23, 2002

Applicant: SGL Carbob AG
65203 Wiesbaden DE

Inventors: Bauer, Moritz, 86153 Augsburg DE
Heine, Michael, Dr.; 86695 Allmannshofen DE
Kienzle, Andreas, Dr.; 86672 Thierhaupten DE
Hüner, Ronald, Dr.; 86674 Baar DE
Rahn, Andreas; 86637 Wertigen DE
Zimmermann-Chopin, Rainer, Dr.; 86679 Ellgau DE

Processes for the manufacture of form assemblies out of fiber-strengthened ceramic materials

Processes for the manufacture of form assemblies out of fiber-strengthened ceramic materials,

whereby in the first step nucleuses are produced a green assembly, in that a compactable mass is filled into a form, whereby the compactable mass of carbon fibers and/or carbon filaments and pitch and/or resin, which carbon-containing residues form at heat treatment under exclusion of oxidizers, contains

in the second step of the green assemblies through warming up on a temperature from 120°C to 280°C under pressure, it is hardened,

in the third step of this also as prepresses indicated green assembly hardened through heating in a not oxidizing atmosphere on a temperature of approximately 750° C until approximately 1100° C for a C/C assembly carbonized becomes,

the heating whereby in the first, second and/or third step at least portion-wisely through it is caused that an electric current through the compactable mass, the green assembly and/or the hardened green assembly is escorted, following this process of produced form assemblies as well as their application as brake -, clutch disks and brake disks

Description

[0001]
The present invention refers to a process for the manufacture of form assemblies out of fiber-strengthened ceramic materials. Specifically, the invention involves strengthened carbon a process for the final-shaped manufacture of a porous fiber-strengthened carbon-containing form assembly, specifically a fiber-reinforced C/C assembly (with carbon fibers, English "CFC" or "CFRC", carbon fibre reinforced carbon) that molded

from binder-containing fiber masses by means of a compression process and in a following thermal treatment for C / C is converted,

just as if necessary the after-compression of this porous fiber-strengthened carbon-containing form assembly under formation of a ceramic molding, specifically through a liquid metal infiltration into the C/C assembly, if necessary with subsequent heat treatment, whereby the molding then contains metals and the metal carbides formed through reaction with the carbon as well as if necessary remains of not converted carbon.

[0002]
The invented process specifically involves the manufacture of ceramic system materials strengthened with carbon fibers, that show removal and cavities if necessary, which at least over the liquid metal infiltration with silicon meltdowns under reaction of a part of the carbon to silicon carbide in with carbon fibers of strengthened system materials with SiC-containing or carbon, SiC-containing molding, and Si-containing molding (C/SiC - or C / C-SiC materials) is converted. These system materials specifically find application at disks, clutch disks and brake disks, as well as as high-temperature-stable construction materials.

[0003]
Nowadays, mainly use materials for disks in the car manufacture are steel or gray casting, and in the aeronautics with carbon fibers of strengthened carbon materials (C/C). the properties demanded by the disk materials are included high mechanical stability, temperature resistance, hardness and wear strength in the rubbing combination of the brake opposite the rubbing partner. The use temperature until now used gray casting disks is limited on that occasion through the melting point of the material. The mechanical defection temperature, dependent on the load, clearly already lies below the melting point. Still, the danger of a rip formation in the disks appears through conversion of the metallic structure when heating. The application of fiber-reinforced ceramics of material for disk applications proves to be solution for this problem. Specifically, materials on the basis of silicon carbide (C/SiC) strengthened with carbon fibers proved to be suitable for this application. The advantages of this material are the lower density, so that lower weight with same volume, the high hardness and temperature resistance to approximately 1400 °C and not least the extremely high wear resistance. This clearly low-density of disks from these C/SiC materials proves as positive influential factor for the improvement of the comfort and the security through the reduction of the springless masses at motor vehicles and as economic factor in the area of the aeronautics. The large hardness and wear resistance of C/SiC prefabricated parts enables much higher stand periods in the comparison for until now usual materials on C/C-Basis or metal basis here.

[0004]
Processes for the manufacture of C/SiC prefabricated parts are known from the writing

DE-A19856721, DE-C19711829 and DE-A19710105, for example, and among other things include the following steps:

Produces a compactable mixture or image-pure mass from carbonic fibers or fiber bundles on the one hand, that can have coated with a coating, and filling means and/or binders like for example resins and/or pitch on the other hand,

Design of the mixture of pressure and temperature and carbonization of the carbon-containing filling means and binder for the manufacture of a form assembly, specifically an out of carbon strengthened with carbon fibers of existing form assembly (C/C) and if necessary graphitization

Silicon melt and at least partial reaction with the carbon infiltrate at least an edge layer of the form assembly with one in the form assembly for sic, whereby a form assembly refines, that sic at least in the edge layer of a system ceramics in a molding from predominant as well, Si and C embedded, carbon-containing fibers exists, here also as C/SiC indicates.

[0005]
In the following one, broadly also the material variation, with which described like above, should be understood only one edge layer siliconized by C/SiC materials becomes.

[0006]
Under an image-pure fiber mass is as well as the fiber-containing compactable masses, that characteristically contain short fibers or short fiber bundle, as also mats, tissue, or mats, that among other things one can process in prepreg technology, summarized. More final is suitable specifically also for it to be virtually or completely molded without force effect

[0007]
Also the ones ones belong for the usual productive techniques, with which the C/C assembly over the liquid phase or gas phase with carbon forerunners ("carbon precursors", substances that form carbon when heating under exclusion of oxidizing media) or with carbon is following-condensed, or the molding from predominant SiC, Si and C through a gas phase infiltration (CVD) Chemical Vapour Deposition, or CVI, Chemical Vapour infiltration, or by the pyrolysis of Si-containing preceramic polymers is generated.

[0008]
When pressing the green assemblies, the heat necessary for the thermal hardening of the binders is brought in into the compactable mass and the workpiece respectively from outside in general in that the press or at least the press form is heated. The more outer area of the workpiece is heated on that occasion on higher temperatures than the

inner area so that the heat can be transported through the temperature gradient into the inside of the workpiece. This uneven heating leads to an uneven hardening and can lead for stressings in the workpiece; the chemical and physical processes running in the more outer zone can lead even also that free-nascent gases cannot escape with the heating and the chemical reactions running with it through the more outer zone, for example, and contribute for bursting of the workpiece or for rips in the workpiece. The total duration of the compression process is moreover, that press cycle time, undesirable high, since heats finished press part vertical in the contact with the pressed material, that a considerable heat capacity possesses occasionally, and must be cooled again. This manifests itself also in a high energy consumption.

[0009]
Goal of the invention therefore is being specifically prepared a process with short cycle times and low energy consumption with the compression process, that is suitable for the manufacture of fiber-strengthened carbon-containing green assemblies or prepresses, that if necessary through infiltration with liquid metals afterwards, liquid silicon and following reaction is specifically transferred in form assemblies out of fiber-reinforced carbidischer ceramics.

[0010]
This goal is solved invented in that such pressed materials are introduced, that show an electric conductivity, that is suitable, before, to develop a part of the heat energy required for the hardening at least heat during or following pressing through conduction of Joule electric current.

[0011]
The invention therefore involves a process for the manufacture of form assemblies from fiber-strengthened ceramic materials, whereby

- in the first step a compactable mass into a molding is filled, whereby the compactable mass of carbon fibers and/or carbon fiber bundle and/or carbon filaments, that were coated with carbon or carbon-containing compounds in preferred sage, and pitch and/or resin, which is thermal hardenable and carbonizable, contains

- in the second step the compactable mass through warming up on a temperature from 120°C to 280°C under pressure for a green assembly is hardened,

- in the third step of the green assemblies through heating in a not oxidizing atmosphere on a temperature of approximately 750°C until approximately 2400°C for one C / C assemblies carbonized and/or graphitized becomes, and if necessary

- in the fourth step of the C/C assemblies under receipt of its form with liquid

metal, whereby a reaction of the carbon portion of the molding of the C/C assembly at least partially runs out with the metal under formation of carbides, it is infiltrated

thereby characterized,

that the heating is caused at least portion-wisely through it in the second or third steps that an electric current through the compactable mass, or the green assembly is escorted. As electrically leading components, carbon fibers essentially step on that occasion, carbon fiber bundle and with carbon of coated fibers on.

[0012]
A sufficient heating through the electric current with the compression process presupposes a balanced proportion between electric resistance and created voltage. The low voltage area is included preferred, characteristically with voltages below from 250V.

[0013]
The compactable mass, the green assembly and / or the hardened green assembly shows an electric conductivity of at least 0.1S/m for it preferentially, specifically in the area of 0.1S/m until 100S/m. the conductivity is preferentially in the area from 1 to 50S/m and especially preferentially in the area from 2 to 10S/m.

[0014]
The conductivity of the pressed material is preferred with the pressing and it is picked itself with the compression process of forming green assemblies in a way that itself with the preferred voltages from up to 150V and currents below 500A the temperatures preferred for the hardening by 100 to 280°C has put in.

[0015]
In a preferred version is introduced in the compactable mass of carbon fibers in form of coated short fiber bundles. Especially preferentially, fibers and fiber bundle respectively with average lengths are in this case with graphitized carbon coated below from 50 mm.

[0016]
As thermal hardenable binder becomes pitch like carbonic tar pitch or petroleum pitch and/or resin like phenol resin, epoxide resin, poly imide, introduced filler-containing mixtures with furfuryl alcohol or furan resin. The compactable masses are cured under temperature effect, prefers with temperatures from 100 to 280°C.

[0017]
Particularly with the application from long-fiberor strengthened malleable masses the thermal hardening can also take place virtually pressure-loosely tissue. This

characteristically is the case with form assemblies produced following the prepreg technique or the laminating. A press device can be given up completely here if necessary.

[0018]
By the carbonization or graphitization of the green assembly, a porous C/C assembly is obtained, that one can further-process. It can rework mechanically for example through drilling, twirl or molding machines or composes for more complex structures on the other hand or is stuck.

[0019]
In further steps, the porous C/C assembly also can hardenable and carbonizable binders with thermal, or following-condenses polymers and again carbonized becomes, about for a material with high-density and higher carbon portion, to reach.

[0020]
The carbon of the C/C assembly becomes in a preferred version of the invented process in a fourth step through a melt infiltration with metals and at least partially converted an if necessary subsequent heat treatment for the corresponding carbides. The melt infiltration with silicon, whereby a part of the carbon, preferentially the carbon in the molding, moves at least for silicon carbide, is preferred; the molding then contains SiC, not converted carbon as well as not converted silicon. It becomes to this C / C assemblies characteristically with silicon powder coated and on temperatures of approximately 1500 until approximately 1800°C in the vacuum heats. According to intended application, it is not included necessarily necessary, the entire C/C assembly in C/SiC, to convert, in general however the edge layer is converted at least for C/SiC. Although the silicon melt infiltration is the preferred process, the C/C assembly can be following-condensed also with other usual processes under formation of the Matrices current in the system material technology. Specifically, the fluid silication process can be executed also with silicon alloys, that among other metals like Cr, Fe, Co, Ni, Ti and/or Mo can contain.

[0021]
The described process can be used preferentially for the manufacture of disks or clutch disks.

[0022]
To this a molding, that shows the desired exterior contours, with the compactable mass is filled and the press form are collided, whereby the electric current is introduced over the cover area and bottom area of the molding into the pressed material. Since the electric resistance of the mass specifically varies with the density during the compression process, is the created voltage or the amperage to be also shaped variably over the entire compression process. In contrast to a heating through heat management from outside becomes hereby an even heating over the cross-section and

over the height the itself of forming green assembly or workpiece reaches.

[0023]
The hardened green assembly then like above is described further-processed, i.e. carbonized and/or graphitized and subsequent through melt infiltration with liquid metals, preferentially liquid silicon, at least partially into the corresponding carbides transfers.

[0024]
In the green state or in the carbonized state, the required drillings can for the attachment of the disks or clutch disks as well as, if desired, cavities and removal for the ventilation through the familiar mechanical treatment processes like drilling, twirl and molding machines into the workpieces is brought.

Patent claims

1.
Processes for the manufacture of form assemblies out of fiber-strengthened ceramic materials, whereby

in the first step a compactable mass into a molding is filled, whereby the compactable mass of carbon fibers and/or carbon fiber bundle and/or carbon filament and pitch and/or resin, which is thermal hardenable and carbonizable, contains

in the second step the compactable mass through warming up on a temperature from 120°C to 280°C under pressure for a green assembly is hardened,

in the third step of the green assemblies through heating in a not oxidizing atmosphere on a temperature of approximately 750°C until approximately 2400°C for a C/C assembly carbonized and/or graphitized becomes,

thereby characterized,

that the heating in the second and/or third step at least partially through it is caused that an electric current with the compression process through the compactable mass and/or the hardened green assembly is escorted.

2.
Processes following claim 1, thereby characterized that subsequent on the third step

in the fourth step of the C/C assemblies under receipt of its form with liquid metal, whereby a reaction of the carbon portion of the molding of the C/C assembly at least partially runs out with the metal under formation of carbides, it is infiltrated.

3.
Processes following claim 1, thereby characterized, that the electric conductivity of the compactable mass amounts to before or during the compression process at least 0.1S/m.

4.
Processes following claim 1, thereby characterized, that the electric conductivity of the green assembly amounts to at least 0.1S/m.

5.
Processes following claim 1, thereby characterized, that the compactable mass is warmed up by conduction of electric current over the cover area and bottom area of a molding.

6.
Porous C/C form assembly, produced one or several of the antecedent claims following the process.

7.
Application of porous C/C form assemblies following claim 6 for the manufacture of C/SiC ceramics through liquid infiltration with silicon or silicon alloys.

8.
Application following claim 7 for the manufacture of brake disks, disks or clutch disks.

9.
Application following claim 7 for the manufacture of ceramic form assemblies for the car manufacture, the construction of air vehicles and spacecraft as well as for the furnace construction.

Translated from the German by
Dr. Max Roha
September 4, 2003

We did not strive for a perfect translation of this document. This document has been translated from the German by automatic computerized translation software. Little effort has been done to optimize the choice of sentence structure and appropriate words. Only a few obvious errors and untranslated words have been corrected. We assume no liability for translation errors. All uses of this document are the responsibility of the client.